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CHEMICAL TECHNOLOGY II

B.Tech (Second Year)

Chemical Engineering

PART 1

CONTENTS

Chapter 1

Phosphorus Industries

The use of artificial fertilizers, phosphoric acid, and phosphate salts and derivatives has increased greatly, chiefly because of aggressive and intelligent consumption promotion on the part of various manufacturers and federal agencies. However, before full consumption of these products could be achieved, more efficient and less expensive methods of production had to be developed. During recent decades, the various phosphate industries have made rapid strides in cutting the costs both of production and distribution and have thus enabled phosphorus, phosphoric acid, and its salts to be employed in wider fields and newer derivatives to be introduced. Supplementing the development of more efficient phosphorus industries have been the pure chemical studies of phosphorus, in its old and in its new compounds. These phosphates are not simple inorganic chemicals, as was assumed several decades ago, and their study has become a unique and complicated branch of chemistry that may some day be compared with the carbon (organic) or silicon branches of today. The properties of phosphorus chemicals are unique because of the important role of phosphorus in many biochemical processes, the ability of polyphosphates to complex or sequester many metal cations, and versatility in forming various types of organic and inorganic polymers.

HISTORICAL. The use of phosphatic materials as fertilizers was practiced unknowingly long before the isolation and discovery of phosphorus by the German alchemist Brand in 1669. As early as 200 B.C., the Carthaginians recommended and employed bird droppings to increase the yields from their fields. The Incas of Peru prized guano and bird droppings on their islands so highly that it was made a capital offense to kill birds. We are also familiar with the use of fish and bones by American Indians in their crude agricultural methods. Bones and guano continued to be the chief sources of phosphorus and phosphoric acid until after the middle of the nineteenth century, but these supplies were and still are limited. In 1842, a British patent was issued to John B. Lawes for the treatment of bone ash with sulfuric acid. This patent marked the beginning of a large acid phosphate industry which became the basis of our domestic fertilizer industry. Soon afterward various grades of phosphate ores were discovered in England. These were first finely ground and applied directly to the soil. It was soon recognized, however, that treatment of these phosphate minerals with sulfuric acid increased the availability and efficiency of the phosphate for agricultural purposes. At present, acidulation with nitric acid or strong phosphoric acid gives enhanced fertilizer values.

PHOSPHATE ROCK

USES AND ECONOMICS. See Table 1.1. The most important use of phosphate rock is in fertilizers. See Chap. 26 on Agrichemical Industries. Table 1 2 is a compilation of phosphate-rock treatment processes. Tricalcium phosphate in raw and/or steamed and degreased bones and in basic slag is also used after grinding as a direct phosphate fertilizer. A small percentage of the former is sometimes treated with sulfuric acid for superphosphate or as a source material for phosphate chemicals. Large tonnages of phosphate rock are converted to phosphorus or phosphoric acid and their derivatives.

Domestic phosphate rocks are essentially fluorapatite admixed with various proportions of other compounds of calcium, fluorine, iron, aluminum, and silicon.

The formula of fluorapatite is $CaF_2 \cdot 3Ca_3(PO_4)_2$, equivalent to $Ca_{10}F_2(PO_4)_6$. This compound is extremely insoluble. The various means for making the P_2O_5 content more soluble, not necessarily in water, but in plant juices (as measured by "citrate solubility"), are manufacture of various superphosphates and the defluorination of fluorapatite by calcination at incipient fusion temperatures of 1400 to 1500°C with silica or phosphoric acid.

The production of phosphate rock is concentrated in Florida with 87 percent of the total; the western states of Idaho, Montana, and Utah contribute 10 percent, and Tennessee 3 percent. In 1980, 54×10^6 t with a value of $1200 million were produced.[1] Table 16.3 shows the various uses of the rock.

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[1] t = 1000 kg.

Table 1.1 Phosphate Rock Statistics (thousand metric tons and thousand dollars unless otherwise specified)

	1977	1978	1979	1980	1981
United States					
Mine production	166,893	173,429	185,757	209,883	183,733
Marketable production	47,256	50,037	51,611	54,415	53,624
Value	$821,657	$928,820	$1,045,655	$1,256,947	$1,437,986
Average per metric ton	$17.39	$18.56	$20.26	$23.10	$26.82
Sold or used by producers	47,437	48,774	53,063	54,581	45,526
Value	$829,084	$901,378	$1,063,517	$1,243,297	$1,212,433
Average per metric ton	$17.48	$18.48	$20.04	$22.78	$26.63
Exports[a]	13,230	12,870	14,358	14,276	10,395
P_2O_5 content	4,251	4,118	4,611	4,554	3,300
Value	$288,603	$297,357	$356,481	$431,419	$373,192
Average per metric ton	$21.81	$23.10	$24.83	$30.22	$35.90
Imports for consumption[b]	158	908	886	486	13
Customs value	$6,079	$24,379	$21,595	$12,856	$420
Average per metric ton	$38.47	$26.85	$24.37	$26.45	$32.31
Consumption[c]	34,365	36,812	39,591	40,791	35,144
World:					
Production	[d]119,310	[d]128,620	[d]132,913	[e]138,333	[f]135,630

[a] Exports reported to the Bureau of Mines by companies.
[b] Bureau of the Census data.
[c] Measured by sold or used plus imports minus exports.
[d] Estimated. [e] Preliminary. [f] Revised.
SOURCE: *Minerals Yearbook 1981*, U.S. Dept. of Interior, 1982, p. 649

Table 1.2 Phosphate-Rock Processing, Products, and By-Products

Process	Raw Materials and Reagents	Main Products and Derivatives	By-products
Acidulation	Phosphate rock, sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, ammonia, potassium chloride	Superphosphate, phosphoric acid (wet process), triple superphosphate, monoammonium phosphate, diammonium phosphate, monopotassium phosphate	Fluorine compounds, vanadium, uranium (limited)
Electric-furnace reduction	Phosphate rock, siliceous flux, coke (for reduction), electrical energy, condensing water	Phosphorus, phosphoric acid, triple superphosphate, various Na, K, NH_4, Ca salts; phosphorus pentoxide and halides	Fluorine compounds, carbon monoxide, slag (for railroad ballast aggregate, fillers, etc.), ferrophosphorus, vanadium*
Calcium metaphosphate	Phosphate rock, phosphorus, air or oxygen, fuel	Calcium metaphosphate	Fluorine compounds
Calcination or defluorination	Phosphate rock, silica, water or steam, fuel	Defluorinated phosphate	Fluorine compounds

*Vanadium is present in appreciable quantities only in the western phosphates.

Table 1.3 Phosphate Rock Sold or Used by Producers in the United States, by Use (thousand metric tons)

Use	1980		1981	
	Rock	P_2O_5 Content	Rock	P_2O_5 Content
Domestic*				
Wet-process phosphoric acid	33,884	10,444	29,085	8,956
Normal superphosphate	333	107	184	60
Triple superphosphate	1,348	436	1,198	378
Defluorinated rock	430	145	492	166
Direct applications	37	8	27	6
Elemental phosphorus	4,083	1,067	4,055	1,049
Ferrophosphorus	190	49	89	22
Total†	40,305	12,256	35,131	10,638
Exports‡	14,276	4,554	10,395	3,300
Grand total†	54,581	16,810	45,526	13,939

*Includes rock converted to products and exported.

†Data may not add to totals shown because of independent rounding.

‡Exports reported to the Bureau of Mines by companies.

SOURCE: *Minerals Yearbook 1981*, U.S. Dept. of Interior, 1982, p. 654.

Phosphate rock, when very finely pulverized, has limited direct use as a fertilizer, chiefly because of the relatively slow availability of the P₂O₅. However, it is mainly used as a raw material for the manufacture of phosphoric acid, superphosphate, phosphorus, and phosphorus compounds.

PROCESSING.[1] In Florida, both hard and pebble rock phosphate are mined. Hard rock phosphate occurs as nodules and boulders in irregular pockets, but its exploitation is limited. The more extensive and cheaply mined pebble deposits occur with an average overburden of 6 m, and their phosphatic value is too low for economical processing. The pebble deposits themselves, called the *matrix*, are from 3 to 9 m thick. This matrix is composed of clay slimes, silica sand, and phosphate pebble. Pebble sizes range from 1 to 27 mm. The overburden is removed and dumped into a previously mined-out cut. Electrically operated draglines remove the matrix and drop it into an excavated area. Hydraulic guns break down the mud in the matrix and wash it into the pump suction, where it is transported through pipes by large sand pumps to the beneficiation plant (Fig. 1.1).

In Tennessee four types of phosphate rock are found, nodular, blue, white, and brown. Only the latter is mined at present, using open-pit, dry methods. The overburden varies greatly and has an average depth of from 1.8 to 2.4 m. Although originally deposited in horizontal strata, in the large western fields layers of phosphate rock have been severely folded, faulted, and elevated by crustal deformations and resemble fissure veins. The rock may contain approximately 75% bone phosphate of lime[2] but, because of admixture with wall material, it usually averages nearer 70% BPL (Table 1.4). Because of its rather soft structure, the rock has a moisture content of 4 to 6%. It is generally mined by underground methods. Western phosphate rock contains anywhere from 50 to 200 g of uranium per metric ton of rock. The complicated and costly recovery process now in use extracts uranium from phosphate rock via wet-process phosphoric acid, and the uranium goes into solution upon treatment with sulfuric acid. After filtration, the bulk of the uranium is found in the acid filtrate. Some is recovered, presumably by an ion-exchange technique. Fluorine and vanadium are also valuable by-products from phosphate rock.

In the Florida pebble district, initially only coarse phosphate rock was recovered, which had a high BPL, whereas the fines, with a much lower BPL, representing about equal tonnage, were wasted. In the 1920s, experimental work was started to develop a froth-flotation process which would increase the BPL of the fines or raw matrix to at least 66 or 68% from about 40% or less. This procedure is frequently spoken of as *beneficiation*, and one of the successful processes currently employed is illustrated in Fig. 16.1. Such upgrading operations are of far-reaching and increasing importance, as easily mined or better-grade deposits of phosphate rock, and other minerals, are becoming exhausted. These operations not only produce a higher grade of product, but allow larger amounts to be recovered, beneficiated, and used, even in the case of such a low-priced product as phosphate rock.

The matrix from the Florida phosphate pebble deposits is received at the beneficiation plant as a slurry. There it is washed to remove clays and fine particles. The +16 mesh pebble product is drained and sent to storage bins as a marketable product. The −16 mesh material is deslimed in hydrocyclones to remove the −150 mesh material, which is predominately

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[1] Slack (ed.), *Phosphoric Acid*, Dekker, 1968; ECT, 2d ed., Vol. 15, 1968, p. 232; Crerar, H₃PO₄ Route Cuts Costs, *Chem. Eng.* 80 (10) 62 (1973).

[2] This is usually abbreviated BPL and actually means tricalcium phosphate, the chief inorganic constituent of bones.
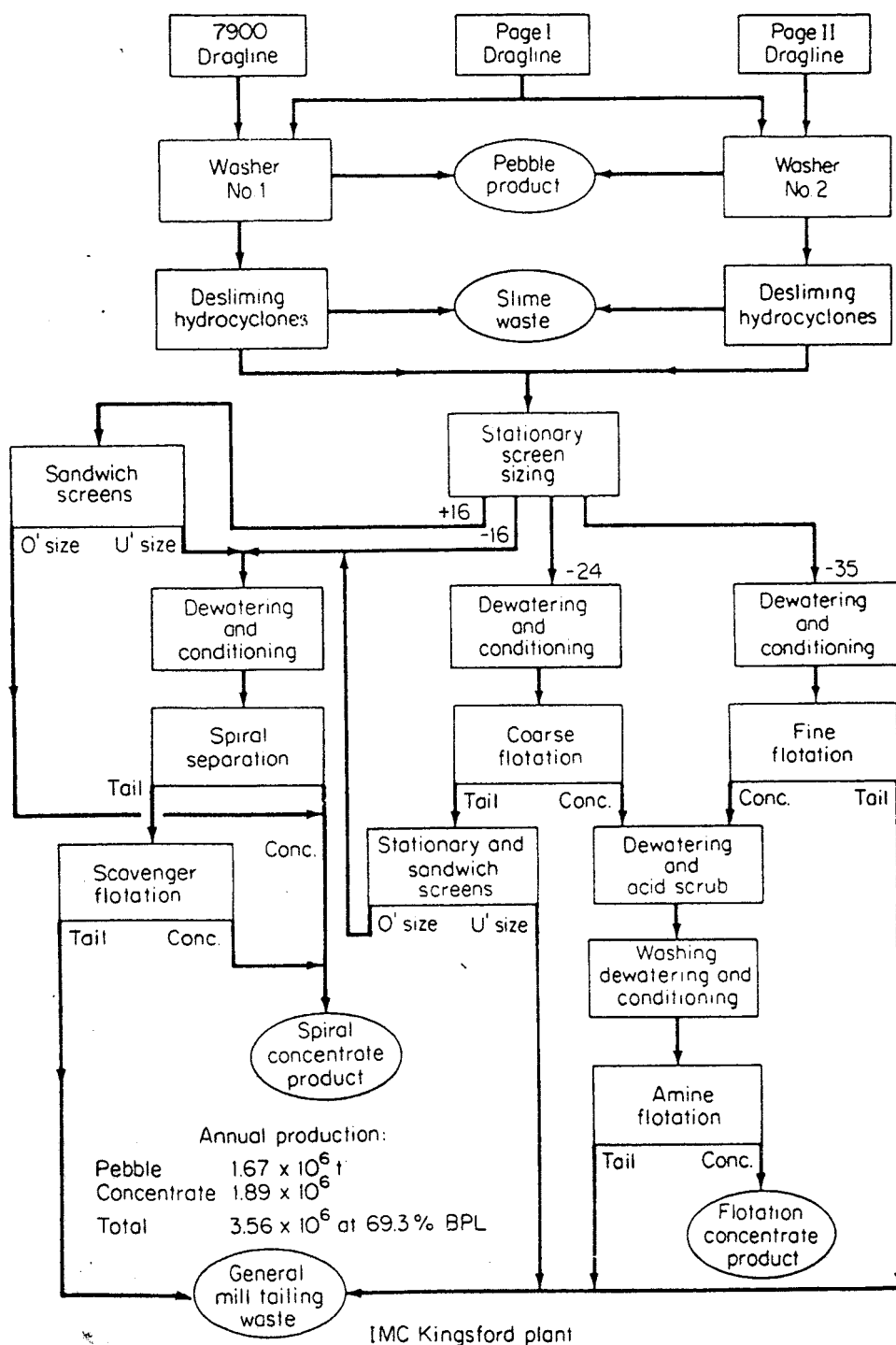
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Washer No 1 → Pebble product ← Washer No 2

Desliming hydrocyclones → Slime waste ← Desliming hydrocyclones

Stationary screen sizing

Sandwich screens — O' size   U' size

+16   -16   -24   -35

Dewatering and conditioning

Dewatering and conditioning

Dewatering and conditioning

Spiral separation

Coarse flotation — Tail   Conc.

Fine flotation — Conc.   Tail

Tail

Scavenger flotation

Tail   Conc.

Conc.

Stationary and sandwich screens — O' size   U' size

Dewatering and acid scrub

Washing dewatering and conditioning

Spiral concentrate product

Amine flotation — Tail   Conc.

Annual production:
Pebble 1.67×10^6 t
Concentrate 1.89×10^6
Total 3.56×10^6 at 69.3% BPL

Flotation concentrate product

General mill tailing waste

IMC Kingsford plant

Fig. 1.1. Florida phosphate rock beneficiation flowsheet. *(International Minerals and Chemical Corp.)*

clays. The -16 to 150 mesh feed is sized on inclined stationary screens. The -16 to 24 mesh fraction is treated as shown in Fig. 16.1 to produce the spiral concentrate product. This is a skin flotation operation using Humphrey spirals.

The froth flotation circuit is separated into fine and coarse floats at 35 mesh because this allows for greater overall recovery of the coarser fractions. Flotation reagents such as saponified fatty acids (soap skimmings) are added. The coarse concentrates are further treated with another flotation step using an amine flotation agent. The final concentrate has a 72 to 78% BPL range.

Table . 1.4 Phosphate Rock Sold or Used by Producers in the United States, by Grade and State in 1981 (thousand metric tons and thousand dollars)

Grade (% BPL* content)	Florida and North Carolina			Tennessee		
	Rock	P_2O_5 Content	Value	Rock	P_2O_5 Content	Value
Below 60	79	17	1,274	698	170	5,732
60 to 66	5,553	1,585	171,443	681	187	11,669
66 to 70	25,727	7,962	639,586	—	—	—
70 to 72	2,984	967	90,303	—	—	—
72 to 74	2,761	929	102,219	—	—	—.
Plus 74	1,371	477	60,015	—	—	—
Total†	38,475	11,938	1,064.839	1379	357	17.401

	Western States			Total United States		
	Rock	P_2O_5 Content	Value	Rock	P_2O_5 Content	Value
Below 60	1783	445	16,999	2,560	632	24.005
60 to 66	907	250	14,243	7,140	2,022	197,354
66 to 70	1614	506	46,353	27,341	8,468	685,939
70 to 72	1368	443	52,599	4,353	1,410	142,902
72 to 74	—	—	—	2,761	929	102,219
Plus 74	—	—	—	1,371	477	60,015
Total†	5672	1644	130,194	45,526	13,939	1,212,433

*1.0% BPL (bone phosphate of lime or tricalcium phosphate) = 0.458% P_2O_5.
†Data may not add to totals shown because of independent rounding.
SOURCE: *Minerals Yearbook, 1981*, U.S. Dept. of Interior, 1982, p. 654.

The waste contains only a small percentage of phosphate ore and is run to a tailing area. Figure 1.2 shows a materials balance flowsheet for the mining and beneficiation of phosphate rock; on average about 4.7 t of product are made per work hour.

SLIME WASTE.[3] The slime wastes from the desliming hydrocyclones occupy about 32 times the initial volume of the rock because of the process water added to separate the matrix from the slime. This volume of waste material plus the tailings from the matrix concentration procedures are impounded by earthen dams. These impounded waste areas (often as large as 320 ha) serve to act as holding tanks to dewater the waste, as reservoirs to minimize water discharge from the mining area, to capture and hold rainwater, and to ultimately densify and store the waste clay. It requires many years to fulfill the design storage level of 25% solids inside the dam.

The phosphate industry currently disposes of 60 percent of these wastes below ground level and is reclaiming mined out land. The holding ponds are not environmentally esthetic and there has been a demand that all these wastes be disposed of below ground level. Because the volume of waste products from mining and beneficiation of phosphate rock exceeds the mined-out volume, this is extremely difficult. Over the past 20 years millions of dollars in

[3]Lawver, The Clay Waste Problem (private communication from International Minerals and Chemical Corp.).
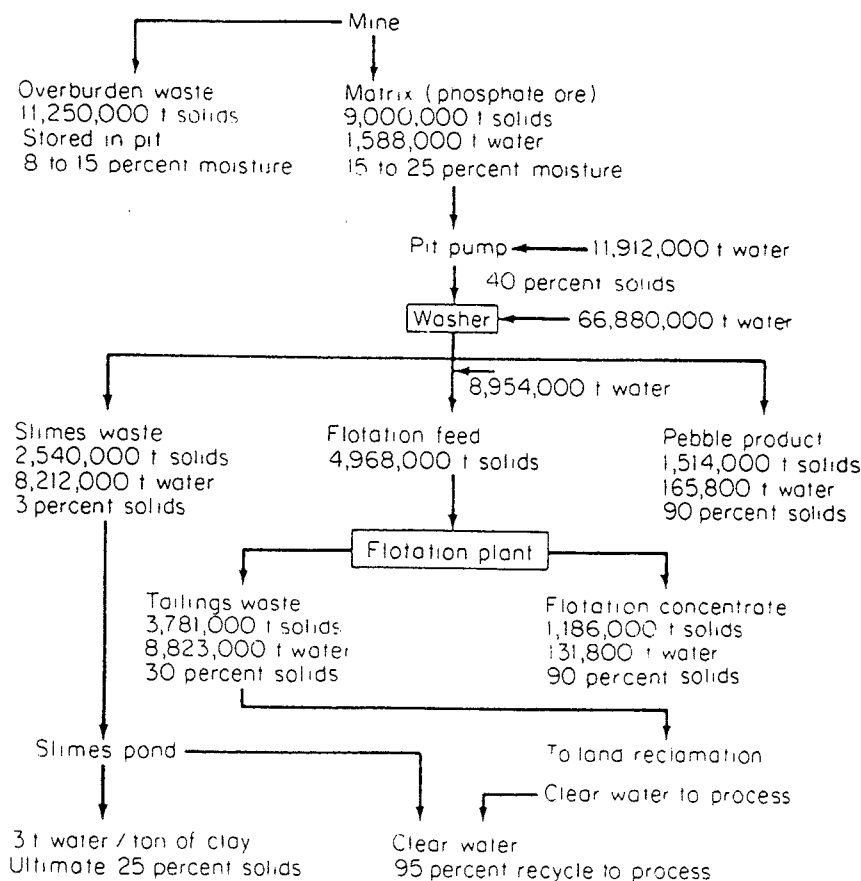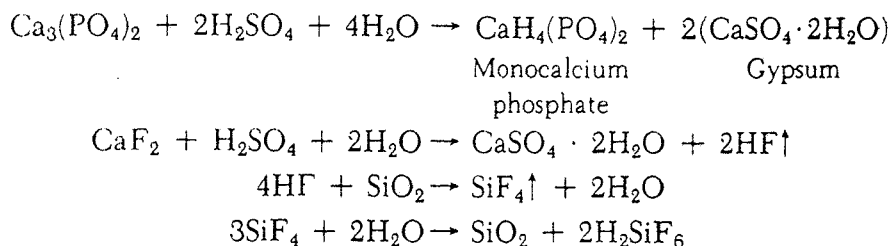
Fig. 1.2. Material balance flowsheet for Florida phosphate rock. Material flow in metric tons per year. *(International Minerals and Chemical Corp.)*

research have been spent in an effort to improve the current waste handling methods. To date no proven large-scale system has been developed that is better, either environmentally or economically.
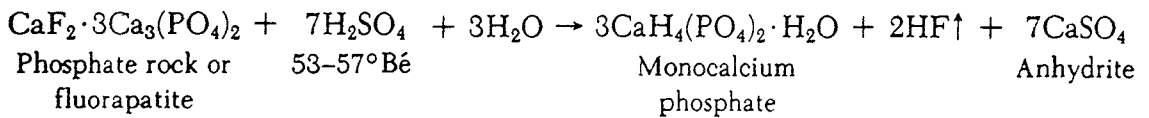
SUPERPHOSPHATES[4]

The acidulation of phosphate rock to produce superphosphate has been the most important method of making phosphate available for fertilizer purposes for nearly a century. See Chap. 26 on agrichemicals. The reactions are

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow CaH_4(PO_4)_2 + 2(CaSO_4 \cdot 2H_2O)$$

$$\text{Monocalcium} \qquad \text{Gypsum}$$
$$\text{phosphate}$$

$$CaF_2 + H_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2HF\uparrow$$

$$4HF + SiO_2 \rightarrow SiF_4\uparrow + 2H_2O$$

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6$$

[4]ECT, 3d ed., vol. 10, pp. 71–76, 1980.

The following is a more probable expression of the main reaction:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 7H_2SO_4 + 3H_2O \rightarrow 3CaH_4(PO_4)_2 \cdot H_2O + 2HF\uparrow + 7CaSO_4$$

Phosphate rock or   53–57°Bé   Monocalcium   Anhydrite
fluorapatite   phosphate

The hydrofluoric acid reacts as shown above, forming fluosilicic acid, but with incomplete removal of fluorine. An excess of sulfuric acid is consumed by such impurities in the phosphate rock as $CaCO_3$, Fe_2O_3, Al_2O_3, and CaF_2. The product increases in weight over the 70 to 75 BPL phosphate rock used, as much as 70 percent resulting in a superphosphate with 16 to 20% available P_2O_5. The manufacture of superphosphate involves four steps: (1) preparation of phosphate rock, (2) mixing with acid, (3) curing and drying of the original slurry by completion of the reactions, and (4) excavation, milling, and bagging of the finished product. Although newer plants use continuous processes, some plants still conduct these operations stepwise. All plants first pulverize the rock. With modern pulverizing and air-separation equipment, most rock is ground to an average fineness of 70 to 80 percent through a 200-mesh screen, with the following benefits: (1) the reaction rate is faster; (2) more efficient use is made of the sulfuric acid and consequently less acid is needed; and (3) a higher grade of product in better condition is obtained.

NORMAL SUPERPHOSPHATE.[5] The continuous process is depicted by Fig. 1.3, where ground phosphate rock (90 percent minus 100 mesh) is fed by a weigh feeder into a double-conical mixer (TVA), where it is thoroughly mixed with metered quantities of sulfuric acid. The sulfuric acid is diluted with water in the cone to a concentration of 51°Bé, the heat of dilution serves to heat the sulfuric acid to proper reaction temperature, and excess heat is dissipated by evaporation of extra water added. The rate of water addition and acid concentration may be varied to control product moisture. The acid and water are fed into the cone mixer tangentially to provide the necessary mixing with the phosphate rock. The fresh superphosphate drops onto the den conveyor, which has a very low travel speed to allow about 1 h for solidifying before reaching the disintegrator. The disintegrator slices the solid mass of crude product so that it may be conveyed to pile storage for "curing," or completion of the chemical reaction, which takes 4 to 6 weeks to reach a P_2O_5 availability acceptable for plant food. The continuous den is enclosed so that fumes do not escape into the working area. These fumes are scrubbed with water sprays to remove acid and fluoride before being exhausted to the atmosphere. The scrubber water is discharged to a limestone bed to neutralize the acid.

Nitric and mixed acid acidulation of phosphate rock.[6] Europe probably first used nitric and mixed acid acidulation of phosphate rock. The substitution of nitric for sulfuric acid is desirable, since nitrogen has an essential value as plant food and can be resold at its purchase price. Simple acidulation of phosphate rock with nitric acid produces a hygroscopic superphosphate, since it contains calcium nitrate. The TVA and others have studied and recommended commercial processes. In one, the phosphate rock is extracted by mixed nitric and

[5]Young and Davis, *The Role of Phosphorus in Agriculture*, chap. 7, ASA-CSSA-SSSA, Madison, Wisc., 1980.

[6]Davis, Meline and Graham, TVA Mixed Acid Nitric Phosphate Process, *Chem. Eng. Prog.*, **64** (5) 75 (1968); Jorquera, Nitric vs. Sulfuric Acidulation of Phosphatic Rock, *Chem. Eng. Prog.*, 64 (5) 83 (1968).
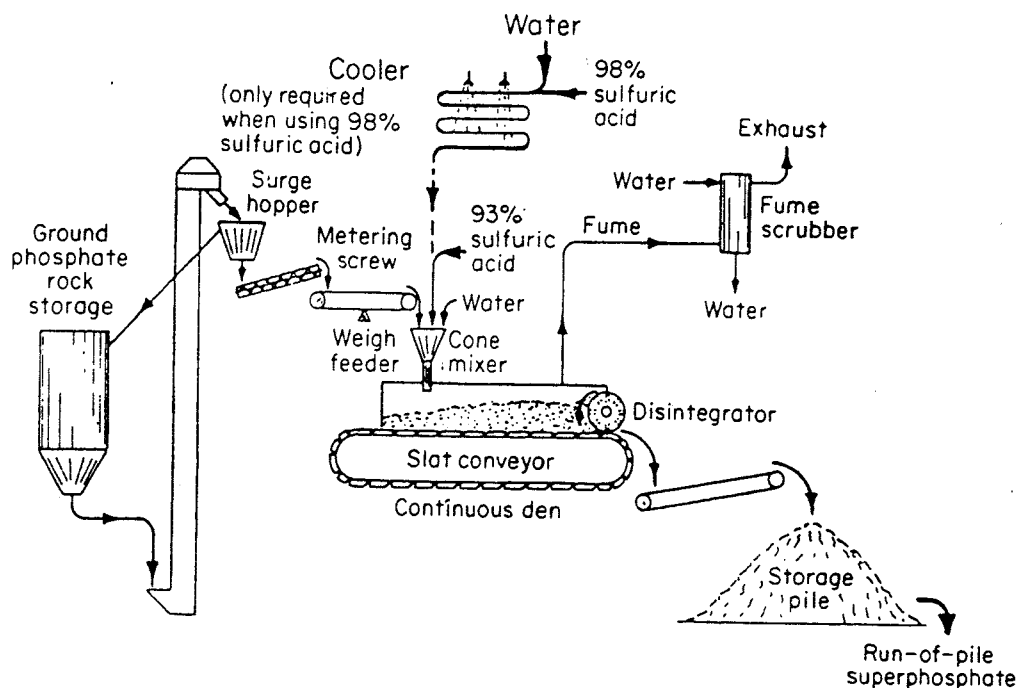
Fig. 1.3. Flowchart for the manufacture of superphosphate. *(Tennessee Valley Authority.)*

sulfuric acids, followed by ammoniation, drying, and the addition of potassium chloride (optional). Another features mixed nitric and phosphoric acidulation, followed by the conventional steps, and others use nitric acid alone for acidulation. These processes, as well as conditioning against moisture absorption as practiced for ammonium nitrate, have led to an extension of the acidulation with nitric acid. Nitrophosphate is also gaining in Europe. Phosphate rock is decomposed with nitric acid plus a small amount of phosphoric acid. The resulting slurry is ammoniated and carbonated and, if desired, combined with potassium salts and spray-dried to yield a uniform pelletized product.

TRIPLE SUPERPHOSPHATE. This material is a much more concentrated fertilizer than ordinary superphosphate, containing from 45 to 46% of available P_2O_5, or nearly three times the amount in regular superphosphate. Triple superphosphate is made by the action of phosphoric acid on phosphate rock; no diluent calcium sulfate is formed.

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 14H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2HF\uparrow$$

The TVA continuous granular triple superphosphate production process is illust Fig. 1.4. Pulverized phosphate rock is mixed with phosphoric acid in a two-st The resultant slurry is sprayed into the granulator. The granulator contain from the process. The product from the granulator is dried, screened, and cooled again. The final product is conveyed to bulk storage whe 4 to 6 weeks during which time a further reaction of acid and rocl the availability of P_2O_5 as plant food. The exhaust gases from the gr scrubbed with water to remove silicofluorides.

Nongranular superphosphate is also available and is prepared using a cone-mixe veyor belt similar to that used to prepare normal (ordinary) superphosphate. As the is only 14 to 20 min as compared with 40 to 50 min for normal superphosphate, a si cupped conveyor belt can be used instead of the slat-type den.
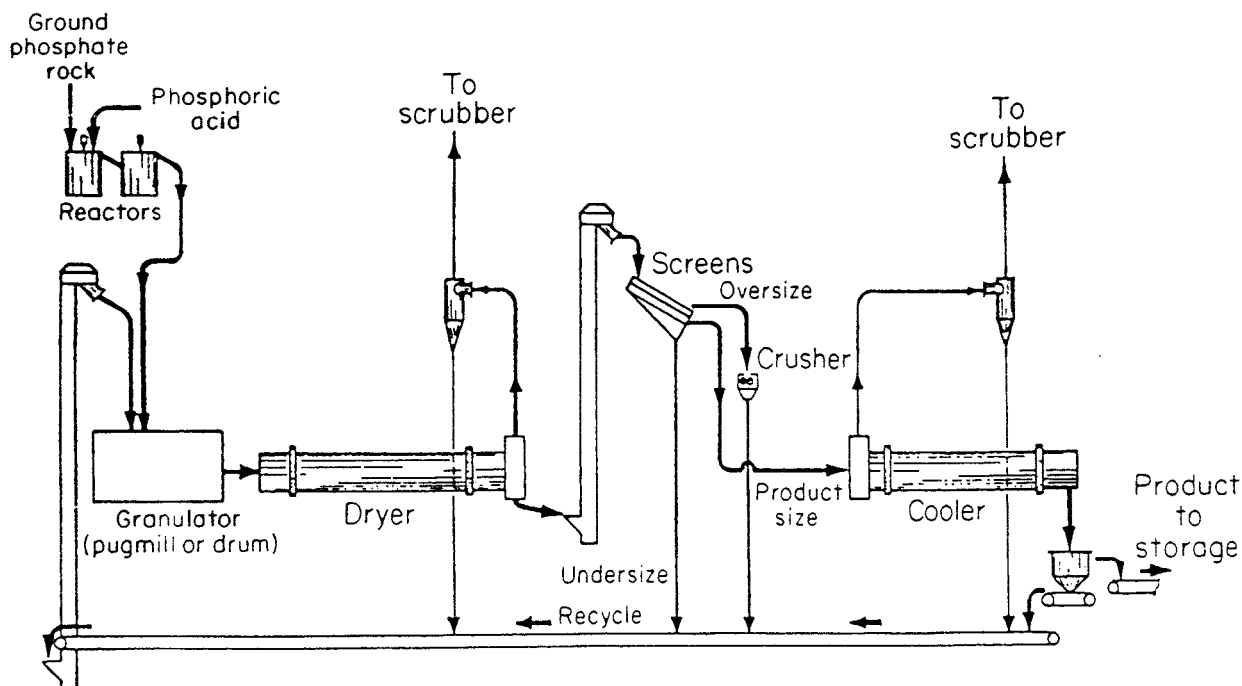
Fig. 1.4. Flowchart illustrating a triple superphosphate process. *(Tennessee Valley Authority.)*

WET-PROCESS PHOSPHORIC ACID

USES AND ECONOMICS. Rapid expansion in the manufacture of wet-process phosphoric acid has resulted from the increased demand for high-analysis fertilizer, triple superphosphate, and ammonium and dicalcium phosphates.

Much earlier, most of the orthophosphoric acid produced was prepared by the action of dilute sulfuric acid, 50°Bé, on ground phosphate rock or bones. This method was supplanted by the Dorr[7] strong-acid process, which produced a strong and economical acid. The equipment must be lined with lead, stainless steel, Hastelloy G, or acid-proof brick, and sufficient time provided in the various agitators for the reaction to go to completion. The temperature in the digester must be kept low enough to ensure the precipitation of gypsum ($CaSO_4 \cdot 2H_2O$), and not anhydrite. If the latter is formed, it subsequently hydrates and causes plugging of pipes. Acid made by this process is used almost entirely in fertilizer production, where impurities are unimportant, or after some purification for various sodium phosphates. Pure acid is obtained from elemental phosphorus by the electric-furnace process.

New methods are being developed to purify wet-process acid by solvent extraction using a mixture of di-isopropyl ether and tributyl phosphate as solvent.[8] This process produces pure enough acid to be used for pharmaceuticals and cattle feed.

The major end uses of phosphoric acid are fertilizer, 85 percent; detergent materials, 5 percent; animal feed, 5 percent; and food, beverages, and dentifrices, 5 percent. Excluding fertilizers, the main outlet for phosphorus derivatives has been in soap and detergent manufacture as various sodium phosphates. Because of their ability to precipitate or sequester lime and magnesia, to emulsify or disperse solids in the detergent solution, and to augment the
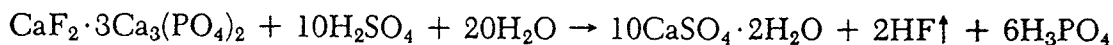
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[7]See CPI 2, p. 353 for flowchart.

[8]Davister and Peterbroeck, The Prayon Process For Wet Acid Purification, *Chem. Eng. Prog.* 78 (3) 35 (1982).
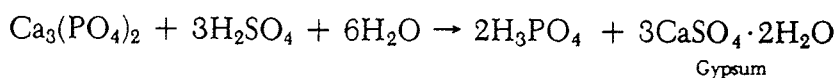
inherent detergent properties of soap and synthetic surfactive agents, these salts have been much used as *soap builders* or *detergent synergists*. Recent concerns about water pollution and algae growth due to the phosphorus content of wastewater have greatly decreased the amount of phosphates in detergents

P_2O_5 production in 1982 was a little over 9×10^6 t of which 8.5 $\times 10^6$ t was wet-process acid and the remainder "furnace" acid.[9] Exports accounted for almost 10^6 t.

MANUFACTURE. The chief process[10] for producing wet-process phosphoric acid is by the use of sulfuric acid as shown in Figs. 16.5 and 16.6. The essential reactions are:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 2HF\uparrow + 6H_3PO_4$$

or, more simply expressed,

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3CaSO_4 \cdot 2H_2O$$
$$\text{Gypsum}$$

Raw phosphate rock, or occasionally calcined rock if a clear, green acid is desired, is digested with sulfuric acid. The retention time ranges from 1.5 to 12 h, and conditions are controlled to produce gypsum crystals that are readily filterable. The reaction is cooled using a vacuum (flash) cooler. The reaction mixture is filtered using a Bird-Prayon tilting-pan filter shown in Fig. 1.6. This process produces 28 to 32% acid which then must be concentrated for most uses.

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[9]Key Chemicals, Phosphoric Acid, *Chem. Eng. News*, 60 (4) 20 (1982).

[10]Fertilizer Needs Spur Wet-Process Phosphoric, *Chem. Eng. News* 45 (12) 54 (1967).
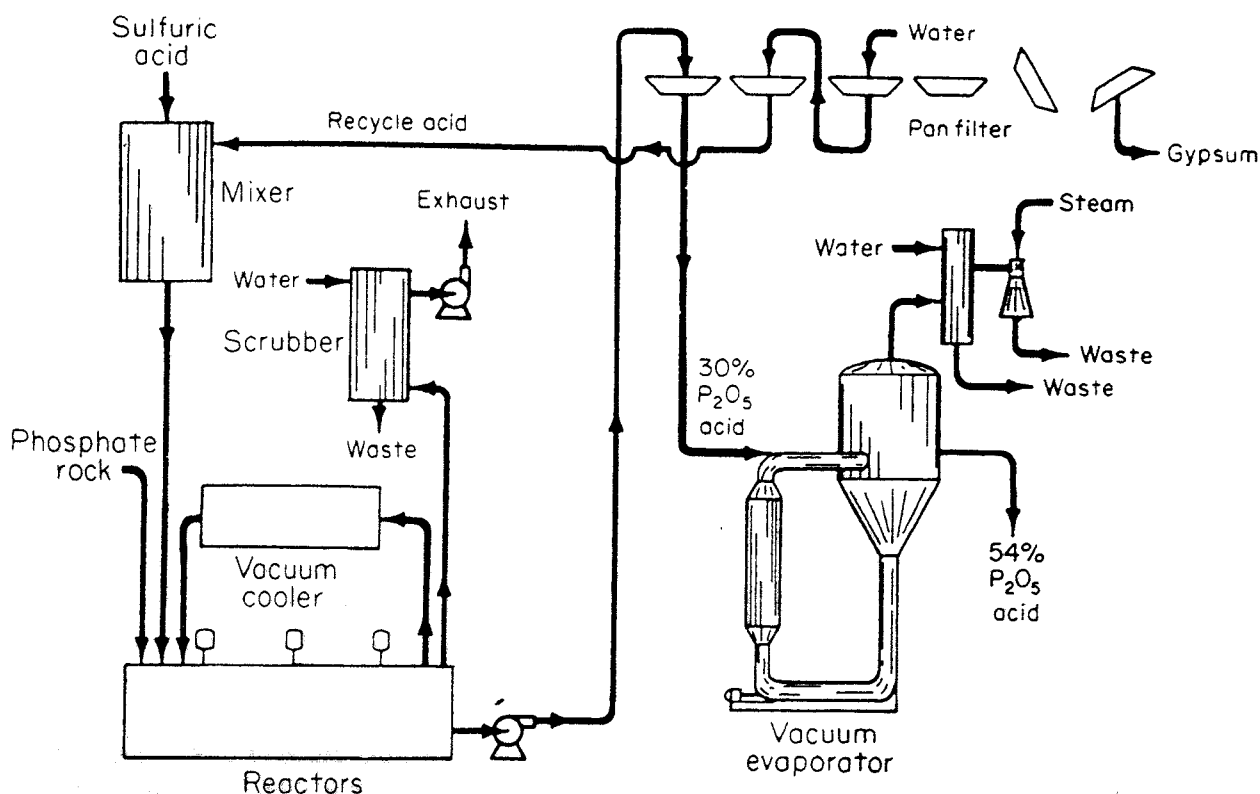

Fig. 1.5. Wet-process phosphoric acid manufacture, using Bird-Prayon tilting-pan washing filters. The overall efficiency is 94 to 98 percent producing an acid of 30 to 32% P_2O_5 concentration.
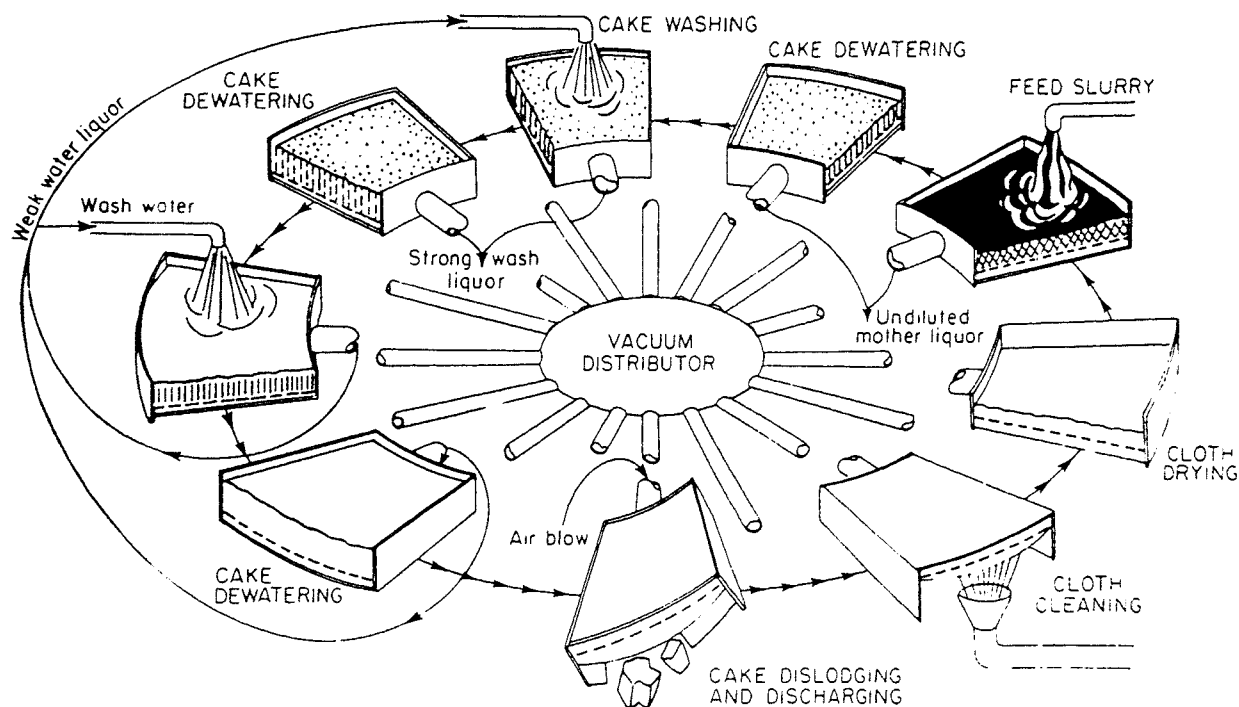
Fig. 1.6. The Bird-Prayon tilting-pan filter for phosphoric acid manufacture. The feed continuously enters the pans, which are connected to the vacuum source. The circular frame supporting the pans rotates so that each pan is moved successively under the desired number of washes. After the final wash liquor has completely drained off, the vacuum is released and the pan is inverted a full 180°. The cake drops off, its removal being ensured by a reverse blast of air through the filter medium, which is then scoured fresh and clean by a high-pressure shower while the pan is still inverted. The filter-medium and drainage area are then purged by vacuum, and the pan returned to the feed position. *(Bird Machine Co.)*

Another process is the Swenson isothermal phosphoric acid reactor which uses a single vessel vacuum crystallizer. The advantages claimed for this process are: reduced capital cost, utilities consumption, and maintenance costs and high operating efficiency with improved P_2O_5 recovery.[11] Recently the idea of producing the calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) instead of the usual dihydrate has been tried.[12] Its disadvantage is that the hemihydrate is unstable and could freeze in the pipes, but the big advantage is that it produces 42 to 50% acid directly without a costly evaporation step as is necessary when the dihydrate is produced. Merchant grade acid is 54%.

Almost all U.S. producers are using the dihydrate process. In 1981 there was only one producer using the hemihydrate process, but as energy costs continue to rise it is expected that more plants will use the hemihydrate process. The potential energy saving is 2.3 to 3.5 GJ/t.

The Haifa process is another method of producing wet-process acid. It uses (1) hydrochloric acid to acidulate (in slight excess to prevent formation of monocalcium phosphate); (2) an organic solvent (C_3 or C_4 alcohols) to extract the phosphoric acid; (3) water to strip out the phosphoric acid (with a small amount of solvent and hydrochloric acid); concentration to

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[11]Olivier, Wet Process Acid Production, *Chem. Eng. Prog.* 74 (11) 55 (1978); ECT, 3d ed., vol. 17, 1982, pp. 426–539.

[12]An Energy Saving Route to Phosphoric Acid, *Chem Week* 128 (2) 46 (1981); Davis, Cogeneration's Place in a Modern Facility, *Chem. Eng. Prog.* 78 (3) 46 (1982); Parkinson, Phosphoric Acid Process Proven for Large-Capacity Plants, *Chem. Eng.* 89 (18) 66 (1982).

remove the small amounts of solvent and hydrochloric acid and to yield a high-grade product. This process was developed in Israel and has been applied in Japan and the United States.[13] The recent dramatic increase in the price of sulfur (from $70 to $140 per metric ton between 1979 and 1981) has renewed interest in the nitric acid process, both for phosphoric acid and superphosphate.

PURIFICATION.[14] Crude wet-process acid is often black and contains dissolved metals and fluorine, and dissolved and colloidal organic compounds. Suspended solid impurities are usually removed by settling. Solvent extraction or solvent precipitation is used to remove the dissolved impurities. Solvent extraction uses a partially miscible solvent, such as n-butanol, isobutanol, or n-heptanol. The phosphoric acid is extracted, and the impurities are left behind. Back-extraction with water recovers the purified phosphoric acid. Solvent precipitation uses a completely miscible solvent plus alkalis or ammonia to precipitate the impurities as phosphate salts. After filtration, the solvent is separated by distillation and recycled

URANIUM RECOVERY.[15] Uranium is present in all U.S. phosphate rocks. Florida rock contains the most, and rock from western states contains the least. It is present as a trace constituent, but because of its high value, it is becoming important to recover it. The methods usually used are solvent extraction of wet-process acid with octyl pyrophosphoric acid (OPPA) in kerosene, extraction with a mixture of tri-N-octyl phosphine oxide and di-2-ethyl-hexyl phosphoric acid (TOPO-D_2EHPA) or use of TOPO-D_2EHPA combined with octylphenyl phosphoric acid (OPAP). The energy value of the uranium extracted, which is converted to yellow cake, U_3O_8, is ten times greater than the energy required to produce it. This could make the phosphate industry a net producer of energy.

In 1981 1.8×10^6 kg of yellow cake was recovered in the United States. This constituted about 10 to 15 percent of the U.S. demand. More than half the demand is potentially recoverable as a result of phosphoric acid production.

ELECTRIC-FURNACE PHOSPHORUS AND PHOSPHORIC ACID

This element was first produced on a small commercial scale by treating calcined bone with sulfuric acid, filtering off the phosphoric acid, and evaporating it to sp gr 1.45. This was mixed with charcoal or coke, again heated, the water evaporated off, then calcined at white heat in retorts. The phosphorus was thus distilled off, collected under water, and purified by redistillation. The production of phosphorus today still depends on volatilization of the element from its compounds under reducing conditions. During the past decades, the method has
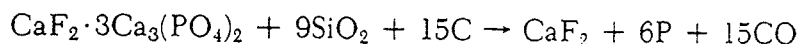
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[13]ECT, 3d ed., vol. 10, 1980, p. 69.

[14]McCullough, Phosphoric Acid Purification, *Chem. Eng.* 83 (26) 101 (1976); Bergdorf and Fischer, Extractive Phosphoric Acid Purification, *Chem. Eng. Prog.* 74 (11) 41 (1978); Davister and Peeterbroeck, The Prayon Process For Wet-Acid Purification, *Chem. Eng. Prog.* 78 (3) 35 (1982).
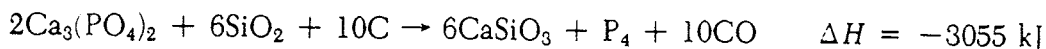
[15]Kouloheris, Uranium from Phosphoric Acid, *Chem. Eng.* 87 (16) 82 (1980); Berry, Recovery of Uranium from Phosphoric Acid, *Chem. Eng. Prog.* 77 (2) 76 (1981). Both articles have excellent flow sheets.

changed chiefly in details and size of production. Elementary phosphorus is manufactured on a large scale as a heavy chemical and shipped in tank cars from the point of initial manufacture, where raw materials are cheap, to distant plants for conversion to phosphoric acid, phosphates, and other compounds.

REACTIONS. Phosphorus is produced by the electric-furnace method (Fig. 1.7). The following reaction is considered to take place, the raw materials being phosphate rock, silica, and coke:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 9SiO_2 + 15C \rightarrow CaF_2 + 6P + 15CO$$

or, more simply expressed,

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4 + 10CO \qquad \Delta H = -3055 \text{ kJ}$$

The silica is an essential raw material which serves as an acid and a flux. About 20 percent of the fluorine present in the phosphate rock is converted to SiF_4 and volatilized. In the presence of water vapor this reacts to give SiO_2 and H_2SiF_6:

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

The fluorine is not recovered by manufacturers of phosphorus, but the CO is employed as a fuel in preparing the furnace charge. The slag tapped from the furnace is sold as ballast, or aggregate or fill. Ferrophosphorus is tapped as necessary, its quantity being dependent on the amount of iron originally in the burden or added to it. The phosphorus is employed usually as an intermediate product, being shipped to consumption centers and there burned or oxi-
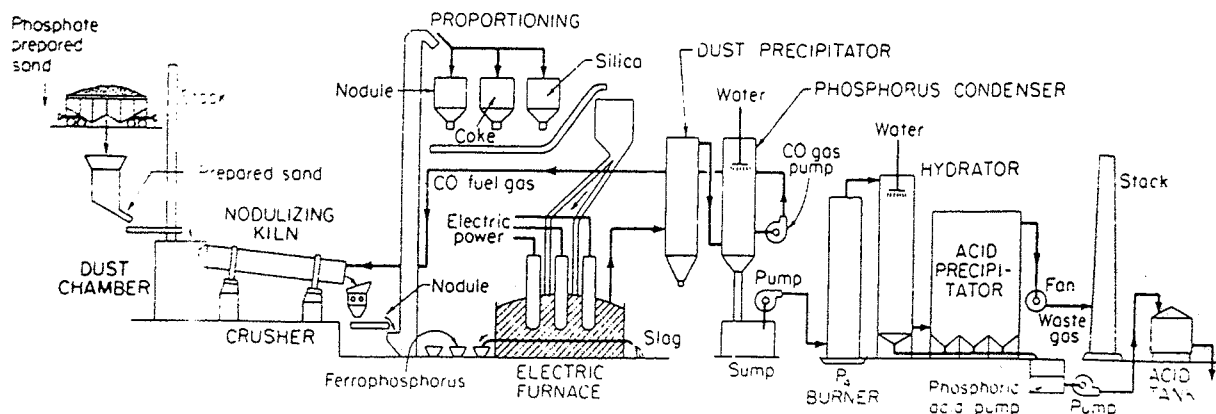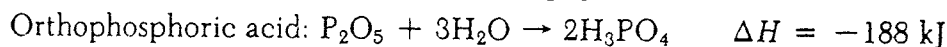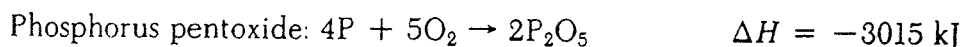

In order to produce 1 t of 85% H_3PO_4, the following materials and utilities are needed:

Phosphate rock (35.6% P₂O₅)	1000 kg	Iron	(depends on ferrophosphorus requirements)
Silica rock	320 kg	Electricity	13,840 MJ
Coke	377 kg	Direct labor (est.)	0.5-1 work-h

Fig. 1.7. Phosphorus production flowchart. In most cases, the hot phosphorus is pumped into an insulated tank car and shipped to the oxidizing plant where it is made into phosphoric acid and various phosphates.

dized to P_2O_5, which is dissolved in water to form acids or other compounds:

$$\text{Phosphorus pentoxide: } 4P + 5O_2 \rightarrow 2P_2O_5 \qquad \Delta H = -3015 \text{ kJ}$$

$$\text{Orthophosphoric acid: } P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \qquad \Delta H = -188 \text{ kJ}$$

The foregoing reactions for ordinary or orthophosphoric acid are commercialized in the following sequences as exemplified by Figs. 1.5 and 1.6 for wet-process acid in comparison with Fig. 1.7 for phosphorus and furnace acid made therefrom.

Wet-Process Phosphoric Acid	Electric-Furnace Phosphorus and Acid
Phosphate rock is finely ground and prepulped in the mixing tank with cooled recycled H_3PO_4 from the slurry cooler.	Phosphate rock ground and sized.
Overflow from the mix tank is reacted with H_2SO_4 and recycled H_3PO_4 in an agitated digester system, forming gypsum crystals and H_3PO_4.	Rock and sand mixed with coke, sintered, and introduced into electric furnace. Mix heated and reduced at an elevated temperature.
Bulk of slurry is recycled through slurry cooler.	Slag and ferrophosphorus run off separately. Phosphorus vapor and CO drawn off, phosphorus condensed.
Rest of slurry is conducted through the filter feed tank to the cells of the rotary Bird-Prayon tilting-pan filtration unit.	Phosphorus transported in tank cars to consuming centers.
In the progressive and tilting pans of this filter, the H_3PO_4 is separated from the gypsum, using three-stage countercurrent washing.	Phosphorus melted and sprayed into stainless-steel oxidation tower. Phosphorus oxidized to P_2O_5.
Gypsum is automatically dumped.	P_2O_5 cooled and hydrated in stainless-steel hydrator or tower against water or dilute H_3PO_4.
Off-gases are scrubbed to remove fluorine before venting.	H_3PO_4 mist-precipitated in electrostatic precipitator or a Brink Mist Eliminator.
H_3PO_4 can be used directly (28–32% P_2O_5) or concentrated	H_3PO_4 filtered and purified.

The electric-furnace[16] process was first employed commercially in 1920. This process permits the use of lower-grade rock than the wet-process phosphoric acid process, since the slag carries off impurities. Indeed, lower grades are frequently preferred because of the better CaO/SiO_2 balance for slag formation. The principal requirement is cheap electricity.

The phosphate rock must be charged in lump form or as +8-mesh (Fig. 1.1). Fine material tends to block the exit of the phosphorous vapors and to cause bridging and uneven descent of the furnace charge, resulting in puffs and the carrying over of excessive quantities of dust. Phosphate lumps may be prepared in the following ways: (1) pelletizing by tumbling or extrusion, (2) agglomeration by nodulizing at high temperatures, (3) sintering a mixture of phosphate fines and coke, and (4) briqueting, with the addition of a suitable binder. After agglomeration, coke breeze and siliceous flux (gravel) are added, and the materials are charged to the electric furnace. Iron slugs are added to the charge if more ferrophosphorus is desired. A flowchart with the quantities required is shown in Fig. 16.7. The bottom of the furnace is composed of carbon blocks, and this lining extends up the wall to a point well

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[16]Curtis, The Manufacture of Phosphoric Acid by the Electric Furnace Method, *Trans. AIChE* **31** 278 (1935); Mantell, *Electrochemical Engineering*, 4th ed., McGraw-Hill, New York, 1960, pp. 523–532 (data and diagram); Highett and Striplin, Elemental Phosphorus in Fertilizer Manufacture, *Chem. Eng. Prog.* **63** (5) 85 (1967); Bryant, Holloway and Silber, Phosphorus Plant Design, *Ind. Eng. Chem.* **62** (4) 8 (1970).

above the slag pool. From this point, a high-grade firebrick lining is used. A domelike steel top with a cast refractory lining caps the furnace. Openings for the electrodes and for introducing raw materials are included here. The electrodes are threaded so as to facilitate replacement as the carbon is consumed. The gases and phosphorus vapor are removed at one end of the furnace. The calcium-rich slag from the furnace is usually tapped periodically and crushed for use in the manufacture of glass, for the liming of soil, and as a roadbed ballast The ferrophosphorus is tapped separately, or it runs out with the slag when it is separated and sold as a phosphorus additive for steel. In this process 80 percent of the fluorine stays with the slag. The small portion that leaves with the gas is absorbed in the water used in condensing the phosphorus.

Pure, strong phosphoric acid is manufactured from elemental phosphorus by oxidation and hydration. See Fig. 1.7 and preceding reactions and sequences for manufacture. The oxidation tower, or chamber, is constructed of acid-resistant brick or stainless steel.[17] Phosphoric acid runs down the walls and absorbs about 75 percent of the P_2O_5 and also heat. This acid is *cooled*, some drawn off, and some recirculated. The remaining 25 percent is passed as a mist to a Cotrell or Brink mist eliminator for collection. Some modern plants produce superphosphoric acid, 76% P_2O_5, equivalent to 105% orthophosphoric acid, with which higher-percentage plant foods can be made, e.g., ammonium polyphosphate, 54% superphosphate. and 10-34-0 liquid fertilizer. Other processing plants produce 75 to 85% orthophosphoric acid, depending on the process for which it is to be used.

Phosphoric acid of high P_2O_5 content consists of mixtures of various phosphates with a certain distribution of chain lengths. Individual molecular species are difficult to prepare. Pyrophosphoric acid ($H_4P_2O_7$) can be obtained only through a slow crystallization process, and above its melting point it rapidly reverts to a distribution of various chain phosphates. If P_2O_5 is carefully dissolved in cool water, most of the phosphate will be in the form of tetra-metaphosphate rings.
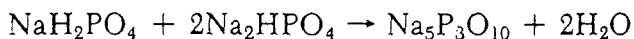
PHOSPHATES

SODIUM PHOSPHATES. The various sodium phosphates represent the largest tonnage of chemicals based on pure phosphoric acid obtained mostly from elemental phosphorus. Phosphates are phosphorus compounds in which the anions have each atom of phosphorus surrounded by four oxygen atoms placed at the corners of a tetrahedron. Chains, rings, and branched polymers result from the sharing of oxygen atoms by tetrahedra. *Orthophosphates* are based on the simple PO_4 tetrahedron as a monomeric unit and include monosodium phosphate (MSP) (NaH_2PO_4); disodium phosphate (DSP) (Na_2HPO_4); and trisodium phosphate (TSP) ($Na_3PO_4 \cdot \frac{1}{4}NaOH \cdot 12H_2O$). The first two sodium salts are made from phosphoric acid and soda ash reacted in the proper molecular proportions; the solution is purified if necessary, evaporated. dried, and milled. TSP is also made from phosphoric acid and soda ash, but caustic soda is necessary to substitute the third hydrogen of the phosphoric acid. These salts are employed in water treatment, baking powder (MSP), fireproofing, detergents, cleaners. and photography (TSP). *Condensed or molecularly dehydrated* phosphoric acids and salts

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[17]Brink, New Fiber Mist Eliminator, *Chem. Eng.* 66 183 (1959); Brink, in chap. 15B, *Gas Purification Processes for Air Pollution Control,* Nonhebel (ed.), Newnes-Butterworths. London, 1972; see Perry, pp. 18-82 to 18-93, for mist collection equipment.

have a H_2O/P_2O_5 molar ratio of less than 3 and greater than 1 and have the single chain unit P-O-P. The best known are the *polyphosphates:* pyrophosphates ($M_4P_2O_7$) and tripolyphosphates ($M_5P_3O_{10}$). When any of the condensed phosphoric acids are dissolved in water, hydrolysis to orthophosphoric acid takes place. Their salts are represented by the widely used sodium tripolyphosphate and tetrasodium and tetrapotassium pyrophosphates.

To produce sodium tripolyphosphate (Fig. 1.8), a definite temperature control is necessary. When MSP and DSP in correct proportions, or equivalent mixtures of other phosphates, are heated for a substantial time between 300 and 500°C and slowly cooled, the product is practically all in the form of the tripolyphosphate.

Figure 16.8 depicts the following coordinated sequences commercializing the reaction:

$$NaH_2PO_4 + 2Na_2HPO_4 \rightarrow Na_5P_3O_{10} + 2H_2O$$

Soda ash and ±75% phosphoric acid are reacted in the mix tank.

The orthophosphates are dried either in a rotary or spray dryer.

The sodium tripolyphosphate is molecularly dehydrated in a gas-fired calciner.

The tripolyphosphate is annealed, chilled, and stabilized in a continuous rotary tempering unit.

The product is milled, stored, and bagged.

Certain equipment modifications have been used, such as addition of an adjustment mixer following the reactor mix tank and a spray tower for drying of the orthophosphate, together with a long, continuous rotary to carry out the dehydrating (calcining), annealing, stabilizing, and cooling in one unit.

PYROPHOSPHATES. Tetrasodium pyrophosphate (TSPP) ($Na_4P_2O_7$), is used as a water softener and as a soap and detergent builder. It is manufactured by reacting phosphoric acid and
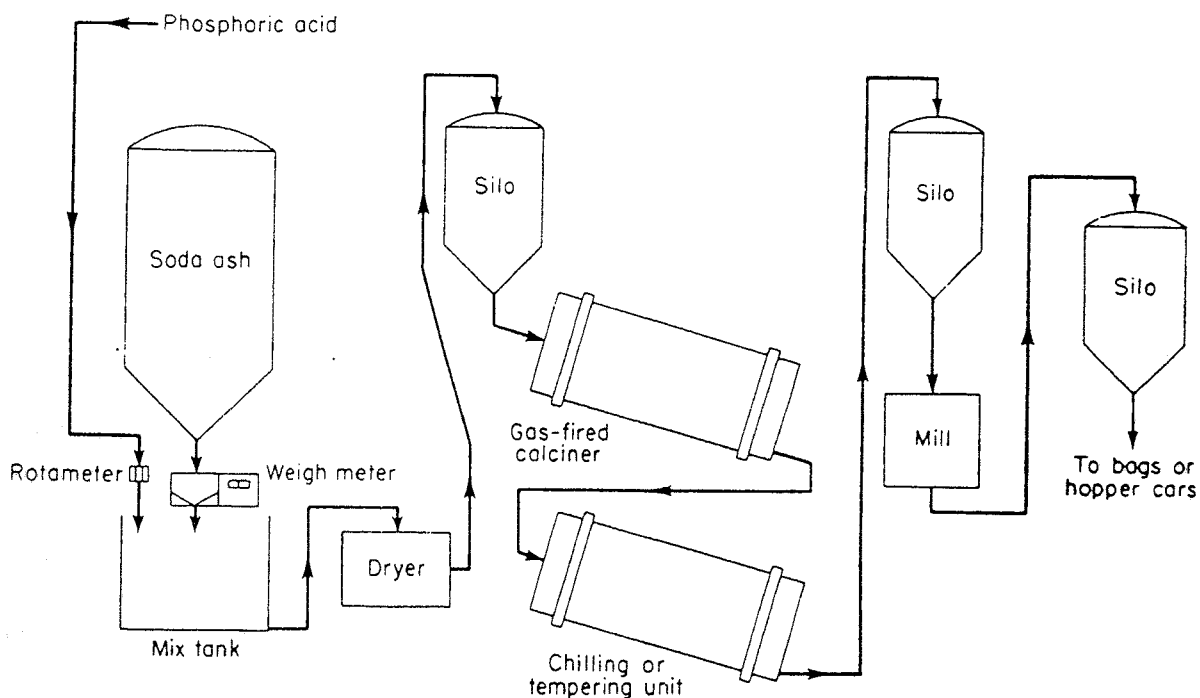

Fig. 1.8. Diagram of a plant for the manufacture of crystalline sodium polyphosphate. *(Thomas L. Hart and John R. VanWazen.)*